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DETERMINATION OF THE CONCENTRATION OF VAPOR GENERATED FROM MONOMERIC 4.4'-DIPHENYLMETHA DIISOCYANATE (MDI) BY A DYNAMIC METHOD

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S u m m a r y

Determination of the Concentration of Vapor Generated from Monomeric 4.4'-Diphenylmethane Diisocyanate (MDI) by a Dynamic Method

In the report by Behlau and Brochhagen dated December 21, 1982 to which reference is made, tests are described to determine the vapor concentration of monomeric MDI generated by bubbling air through a modified grade of monomeric MDI (Desmodur PF). The extrapolation of the data obtained at higher temperatures led to the conclusion that a concentration of monomeric MDI vapor of approx. 0.09 mg/m^3 could be reached at 25°C.

Additional tests have been made using a slightly modified vapor generation equipment and by replacing the modified MDI grade by a pure monomeric MDI in flake form (Desmodur 44 M). Dry nitrogen was used as carrying agent; the sample volume was varied between 60 - 600 l/h.

The temperatures chosen for these studies were 20°C, 25°C, 35°C, 40°C, 50 60°C and 70°C. The analytical evaluation of the MDI vapor concentration was performed by hydrolysing the isocyanate in a mixture of sulfuric acid and dimethyl sulfoxide and by determining the resulting amines using HPLC. In addition several photometric determinations have been made using the Marcali principle.

As the following table shows the average concentrations of MDI vapor were as follows:

	HPLC	Photometry
20°C	0.04 mg/m^3	-
25°C	0.09 mg/m^3	0.08 mg/m^3
35°C	0.26 mg/m^3	0.25 mg/m^3
40°C	0.5 mg/m^3	0.5 mg/m^3
50°C	1.9 mg/m^3	2.0 mg/m^3
60°C	4.7 mg/m^3	5.1 mg/m^3
70°C	10.9 mg/m^3	12.5 mg/m^3

It is evident that the concentration which was determined at room temperature is in good correlation to the figure which was obtained by extrapolation from the data as described in the December 21, 1982 report.

Phenylisocyanate was not detectable in the batch of monomeric MDI used for this study (gas chromatography, detection limit 0.0002 %). There was no indication at the various temperatures that the concentration of phenylisocyanate vapor exceeded 10 % of the total isocyanate vapor (relative detection limit 0.005 mg/m^3 for a sample volume of 1000 l nitrogen).

Determination of the Concentration of Vapor Generated from Monomeric 4.4'-Diphenylmethane Diisocyanate (MDI) by a Dynamic Method

1. Introduction

In connection with the preparation of the long-term toxicity study of monomeric MDI it should be established whether a saturated MDI vapor - free of aerosols - could be obtained at room temperature. Since 40 m^3/h of air having ambient relative humidity and temperature are to be introduced into the inhalation chamber it is evident that this goal can only be achieved by generating a saturated MDI vapor at elevated temperatures using dry nitrogen and diluting it with humid air at normal temperature up to the necessary degree. Trials to generate vapor at elevated temperatures were performed. In order to get an idea about the concentration obtainable at room temperature several tests were made also to generate MDI vapor below 40°C.

2. Test Material

The tested material was Desmodur 44 M (monomeric MDI in flake form). The product had the following specification:

Content of diphenylmethane diisocyanate:	≙ 99.5 %
Melting point:	≙ 38.2°C
Content of 2.4'-MDI:	≙ 3 %

3. Apparatus

For the generation and absorption of MDI vapor an apparatus was used as shown in figure 1.

Dry nitrogen ($<$ 30 ppm O_2) is obtained by cooling the nitrogen from the factory distribution net in a trap (- 78°C); it is passed subsequently through a drying tower filled with blue gel and finally warmed up to the working temperature by a heated coil condenser.

To assure a better dispersion of the carrier gas the introductory tube is perforated at its spherical end.

The molten monomeric MDI is moved by a magnetic stirrer during the introduction of gas. The inlet tube plunges 2 - 3 cm into the liquid. In case of temperatures of 35°C and below the nitrogen is blown through the MDI flakes which are still solid at these temperatures. The vapor leaves the generator about 20 cm above the surface and is carried through a condenser (40 cm in length) which is coupled to a filter, consisting of 1 or 2 glass frits (porosity G 3) embedded in a glass jacket. Condenser and filter serve to separate liquid drops if there are any.

Behind the filter the nitrogen, containing the MDI vapor, is passed through a midget impinger which is filled with an absorption solution described in para 5.

A reflux condenser is connected to this type of washing bottle. The total gas volume (sample volume) is measured by a gasmeter behind the reflux condenser. This serves also to determine the flow rate. All units of the apparatus carrying vapor are jacketed and can be heated by thermostated water. The working temperature is measured close to the filter.

4. Experimental

200 g of Desmodur 44 M are placed in the generator. Nitrogen is blown through the product at a defined temperature (20°C, 25°C, 35°C, 40°C, 50°C, 60°C, 70°C).

The flow rate can be adjusted between 1 and 10 l/min (60 - 600 l/h); the time necessary for one experiment depends on the attainable concentration and varies between 0.5 and 15 h. After the "bubbling" has been finished the absorption solution was analyzed according to the following method.

5. Analytical method

The hydrolysis of aromatic isocyanates to the appropriate amines is a well known method in air analysis[1]. After diazotization the amines are coupled with suitable aromatic compounds and determined photometrically as azo-dyes. These methods only record the total content of aromatic amines and isocyanates and are not suitable to separate individual components.

Taking into account that the monomeric MDI contains phenylisocyanate (PhI) as impurity high performance liquid chromatography (HPLC) was chosen for the analytical determination. This method allows the separate determination of these components in the test atmosphere in the form of the respective amines obtained by acidic saponification, i.e. MDI as diaminodiphenylmethane (MDA), PhI as aniline.

The absorption solution consists of concentrated sulfuric acid and dimethylsulfoxide (1 : 1 v/v, about 13 ml). After the run the midget impinger is thoroughly rinsed with distilled water. The combined solutions are rendered alkaline by adding NaOH and extracted three times with 15 ml portions each of methylene chloride. The solvent is dried over sodium sulfate and transferred to a 50 ml volumetric flask which is completed to volume with methylene chloride.

30 µl of this solution are applied to the HPLC column (ODS-Hypersil, 5 µm, 15 cm) and analyzed according to a gradient program.

Figure 2 shows a typical chromatogram.

The evaluation is performed by the method of external standard:

$$C = \frac{A \times F \times 50000 \times 1.26}{30 \times V} = 2100 \times \frac{A \times F}{V}$$

C = concentration of MDI vapor in mg/m^3
A = area units
F = amount in µg/area unit (response factor)
V = sample volume of nitrogen in l
1.26 = conversion factor (MDA to MDI)

F depends on the area corresponding to the amount of injected substance (Fig. 3).

Control experiments were performed photometrically (see 1, reference 39) using 2-naphtol as coupling agent.

Under our working conditions the calibration of this method led to the following correlation between absorbancy (A) and the amount of MDI:

A (495 nm, 10 mm) x 18 = µg MDI/sample volume

(The general calibration factor F is 139, that is the absorbancy of 1 mg of MDI as azo-dye dissolved in 1 ml of pentanol at 1 cm cell thickness.)

The experimental data are listed in tables 1 and 2. The complete absorption of MDI in one washing bottle was confirmed in preliminary experiments by using two combined bottles. The amount of MDI in the second bottle was found to be far less than 10 % of the amount in the first one. This is within the scope of experimental error. The investigation was performed at various flow rates and temperatures.

6. Results

From tables 1 and 2 it can be seen that the concentration of MDI vapor does not depend on the flow rate between 60 - 600 l/h. In accordance with the results from BROCHHAGEN and BEHLAU[2] it can be concluded that the nitrogen stream is saturated with MDI at all test conditions.

It becomes further evident that the correlation of chromatographic and photometric data is acceptable. Phenylisocyanate (via aniline) was never detectable (relative detection limit 0.005 mg/m^3 for 30 µl of injection volume, 50 ml sample of solution, 1000 l of nitrogen sample volume).

Hence the content of PhI in the isocyanate vapor at 20°C does not exceed 10 % of the MDI vapor concentration. At higher temperatures the PhI/MDI ratio is even smaller.

Figure 4 illustrates graphically the dependence of the MDI vapor concentration on the temperature.

In figure 5 the ln C of MDI vapor is plotted against the reciprocal temperature. The correlation is practically linear (correlation factor r = 0.999).

7. Discussion

The total amount of air to be introduced into the inhalation chamber for the toxicological study is approx. 40 m^3/h. If one assumes that a maximum MDI vapor concentration of 0.05 mg/m^3 can be achieved at ambient temperature a total amount of 2 mg of MDI vapor/h has to be introduced into the chamber. As shown by the study a MDI vapor concentration of approx. 5 mg/m^3 can be expected at 60°C. If therefore 400 l nitrogen, containing MDI vapor generated at 60°C, are diluted with approx. 40 m^3 of air (ambient temperature and humidity) the aforementioned MDI concentration of 0.05 mg/m^3 could be expected.

It must be noted that this calculation is theoretical and disregards a possible adsorption/reaction of MDI vapor on surfaces of the chambers etc.

The exact parameters for the vapor generation for the long-term study will be evaluated in a further investigation by CIVO. The technical concept has been described in the note by Dr. W. Stieler of March 14, 1983.

8. Literature

(1) Technical Information No. 5, Analysis of Isocyanates in Air, International Isocyanate Institute, Inc., 1982

(2) Dr. F.K. Brochhagen, DI F.G. Behlau, report December 21, 1982

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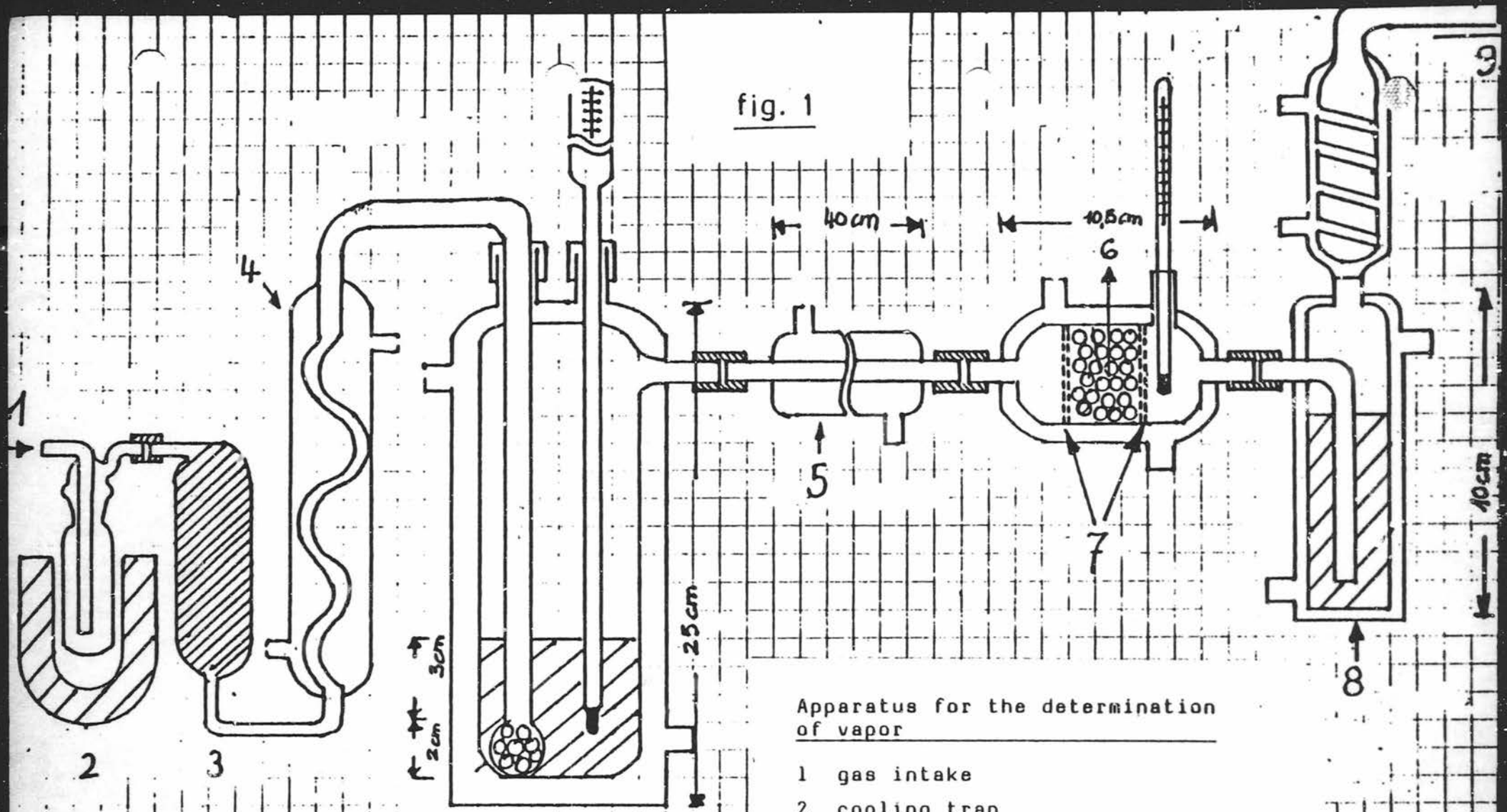
fig. 1



Apparatus for the determination of vapor

1 gas intake
2 cooling trap
3 drying tower
4 heated coil condenser
5 heated condenser
6 glass balls
7 glass frits (porosity: "G.3")
8 washing bottle
9 to gasmeter

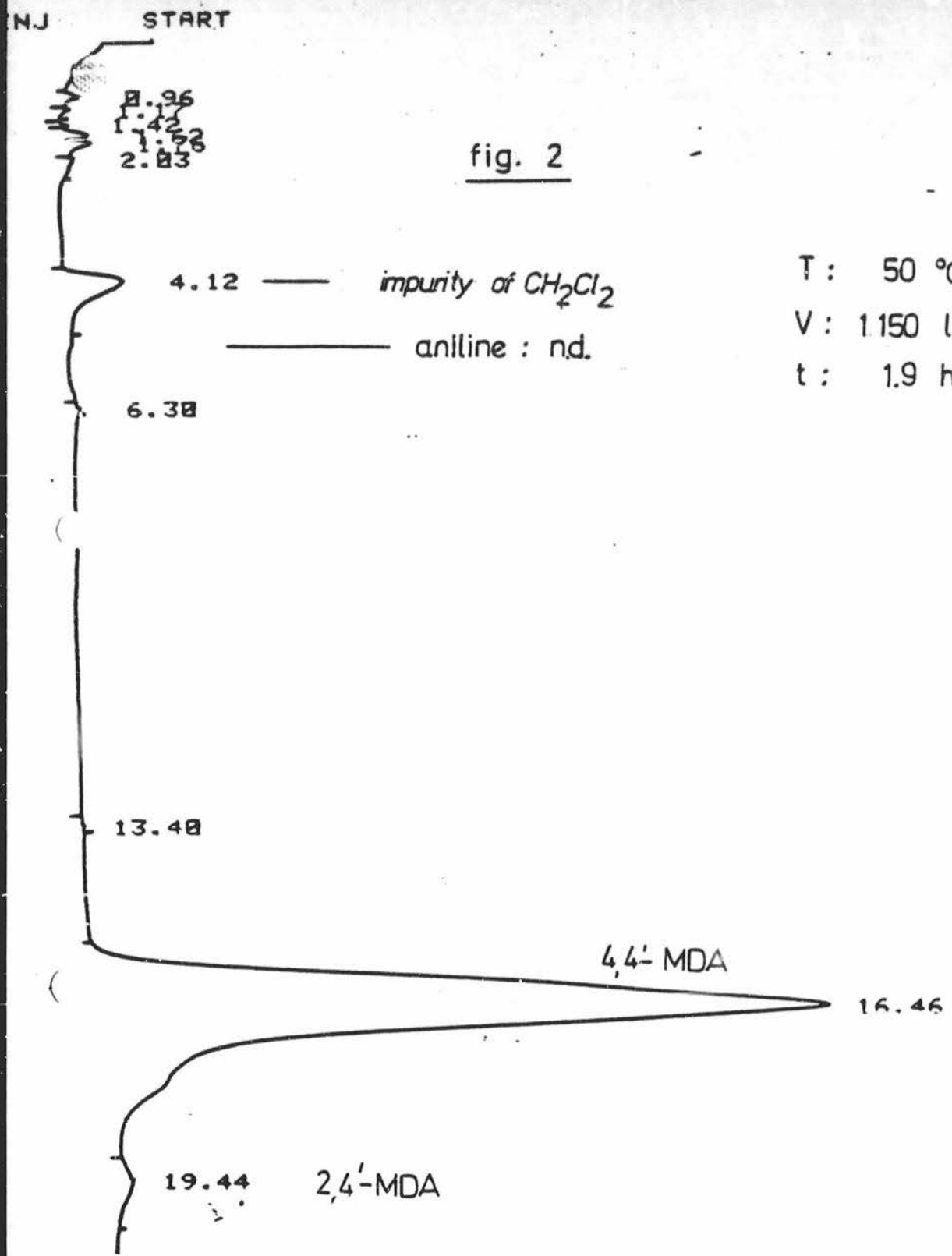


fig. 2

T : 50 °C
V : 1.150 l
t : 1.9 h

BTL: 30
ID:19.05.83-33
NORM FILE 1

RT	EXP RT	AREA		CAL #	AMT
0.96		819			0.207
1.62		1610			0.408
1.76		2272			0.575
2.03		1024			0.259
4.12		12130			3.072
16.46	15.71	365700	R	1	92.611
19.44	19.44	7642		3	2.867

DF: 1.0000 E+ 0

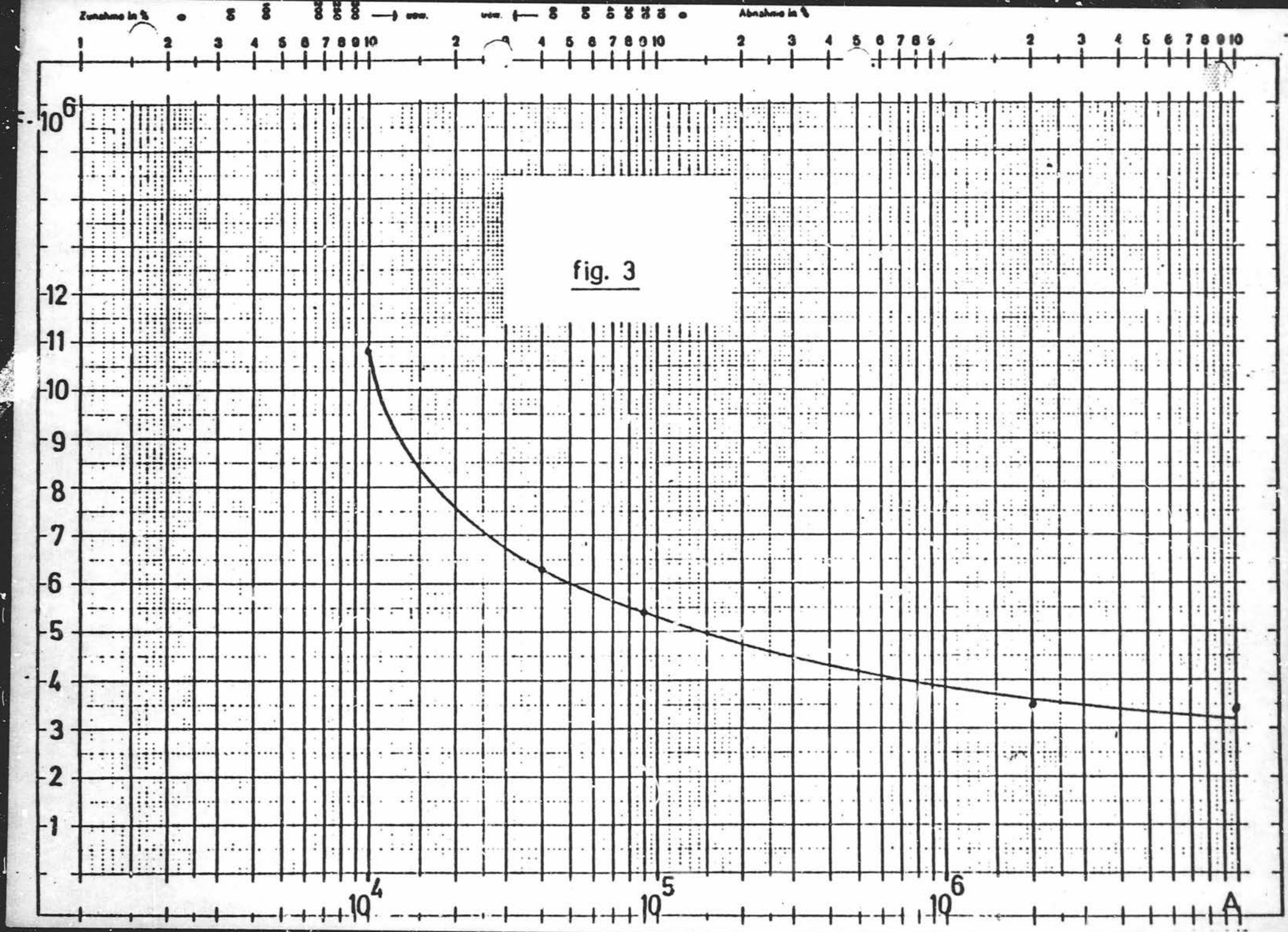


fig. 3

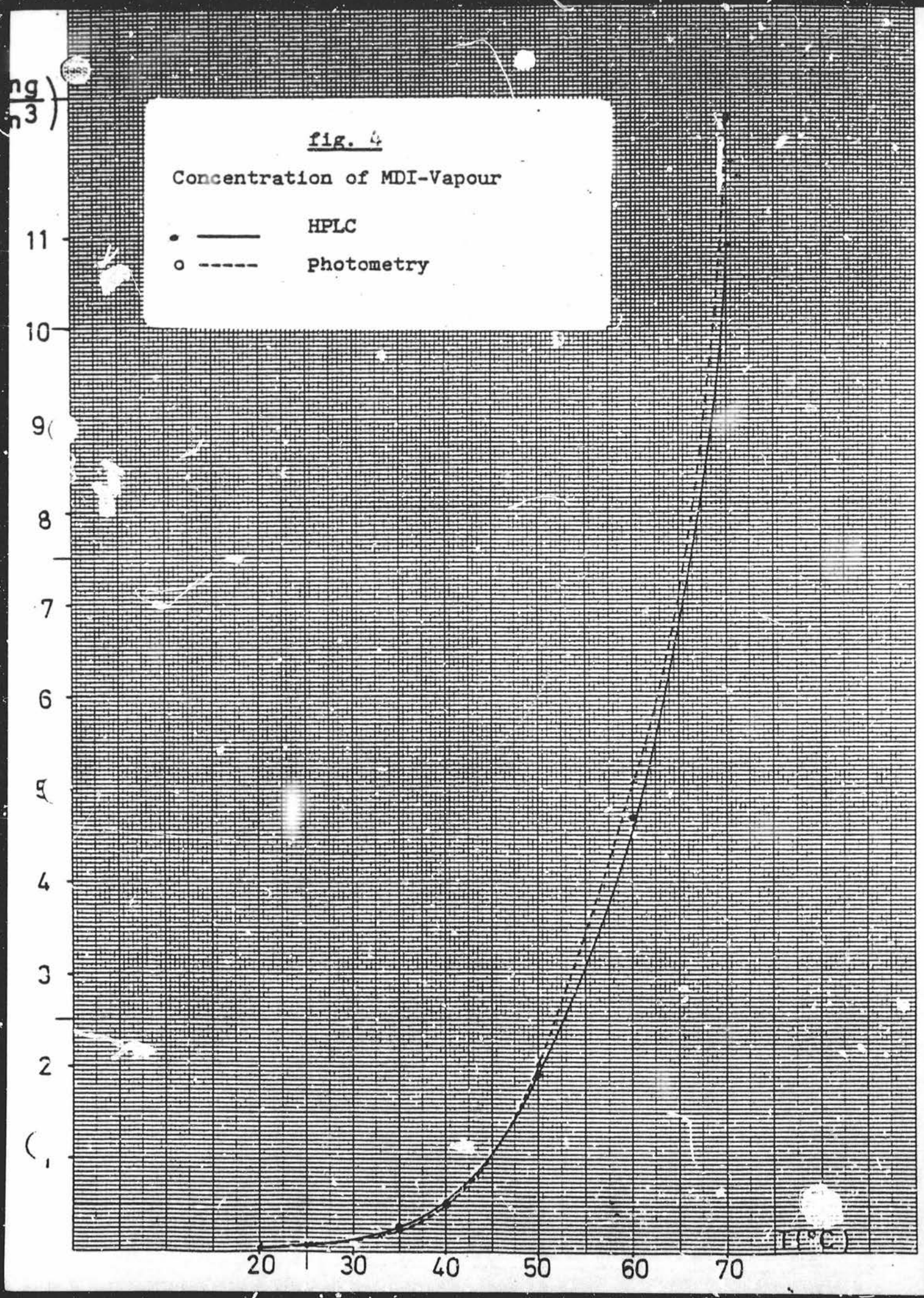


fig. 4
Concentration of MDI-Vapour
HPLC
Photometry
11
10
9
8
7
6
4
3
2
20
30
40
50
60
70

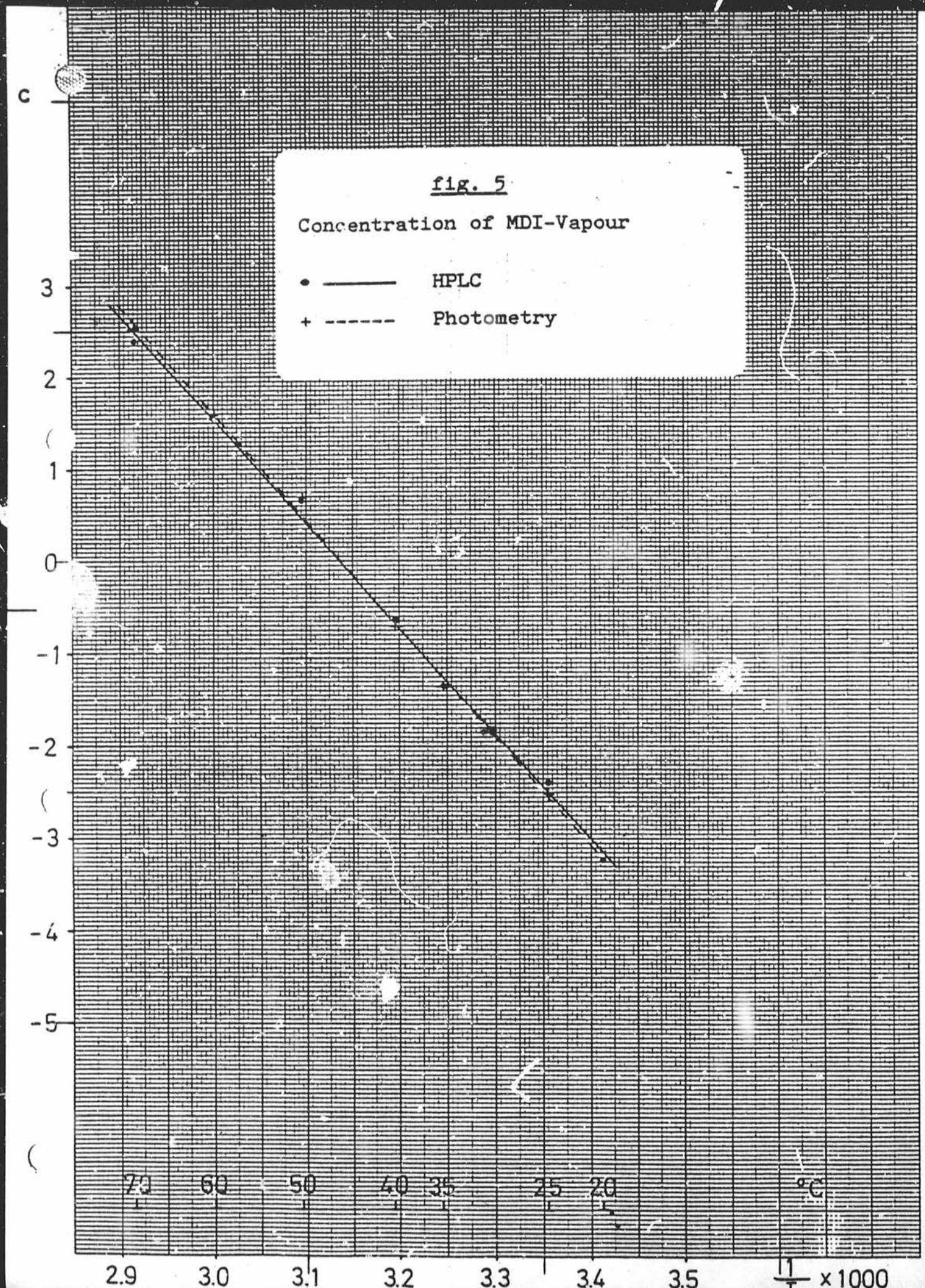


fig. 5
Concentration of MDI-Vapour
HPLC
Photometry
c
3
2
1
0
-1
-2
-3
-4
-5
70
60
50
40
35
25
20
°C
2.9
3.0
3.1
3.2
3.3
3.4
3.5
1/T x 1000

Table 1 (data obtained by HPLC)

°C	Sample Volume (l)	Flow Rate (l/h)	Concentration of MDI Vapour (mg/m3)	
20	1661	104	0.062	
	1890	540	0.019	
		ar.mean	0.04	(lnC= -3.22)
25	8510	540	0.045	
	8120	522	0.040	
	7180	456	0.076	
	8670	534	0.116	
	12503	468	0.120	
	7290	474	0.14	
		ar.mean	0.09	(lnC=-2.41)
35	1420	642	0.171	
	2110	558	0.279	
	2110	540	0.340	
		ar.mean	0.26	(lnC= -1.34)
40	197	60	0.57	
	90	72	0.85	
	130	132	0.58	
	330	180	0.69	
	270	270	0.48	
	250	336	0.57	
	330	396	0.35	
	460	462	0.46	
	460	462	0.43	
	330	660	0.45	
	660	660	0.45	
	560	780	0.56	
	750	804	0.44	
		ar.mean	0.53	(lnC=-0.63)
50	139	60	2.05	
	200	132	2.28	
	220	186	1.81	
	270	228	2.10	
	330	276	1.90	
	460	354	2.06	
	480	408	1.75	
	432	498	1.73	
	607	606	2.01	
	1140	558	1.55	
	1150	606	1.86	
		ar.mean	1.92	(lnC=0.65)
60	130	60	4.40	
	70	72	(6.35)	
	170	132	4.60	
	415	210	4.19	
	190	306	4.51	
	480	372	3.90	
	180	402	4.77	
	990	540	5.78	
	600	600	5.35	
		ar.mean	4.69	(lnC=1.55)
70	260	102	11.34	
	320	486	10.62	
	1000	498	11.29	
	500	600	10.35	
		ar.mean	10.88	(lnC=2.39)

Table 2 (data obtained by photometry)

T°C	Sample Volume (l)	Flow Rate (l/h)	Concentration of MDI Vapour (mg/m³)	
25	2980	187	0.091	
	3230	205	0.070	
		ar.mean	0.08	(lnC=-2.51)
35	850	234	(0.68)	
	560	263	0.30	
	900	262	0.25	
	670	349	0.21	
		ar.mean	0.25	(lnC=-1.39)
40	400	161	0.42	
	650	183	0.58	
		ar.mean	0.50	(lnC=-0.69)
50	130	98	1.94	
	230	108	2.10	
		ar.mean	2.02	(lnC=0.70)
60	70	121	5.02	
	75	104	5.09	
		ar.mean	5.06	(lnC=1.62)
70	20	71	14.2	
	21	78	(17.3)	
	21	60	12.4	
	25	78	11.4	
	23	77	12.0	
		ar.mean	12.5	(lnC=2.53)

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